

## **APPENDIX E**

### **Use of SO<sub>2</sub> Reducing Catalyst Additives to Reduce SO<sub>2</sub>**

This program to reduce SO<sub>2</sub> emissions at each relevant FCCU shall consist of the following steps: baseline data collection and emission model development; a trial period to evaluate the effectiveness of alternative SO<sub>2</sub> reducing catalyst additives; an optimization period to determine optimized addition rates of the selected SO<sub>2</sub> reducing catalyst additive; and a demonstration period to establish appropriate SO<sub>2</sub> concentration based emission limits for the FCCU. On or before the dates specified in Section 7 below for the relevant FCCU, Valero shall commence the activities identified in this appendix.

#### **1. Definitions**

- a. "Baseline Total Catalyst Addition Rate" shall mean the daily average Total Catalyst, in pounds per day, added to an FCCU during the baseline period of an SO<sub>2</sub> catalyst additive program.
- b. "Hydrotreater Outage" shall mean the period of time during which the operation of an FCCU is affected as a result of hydrotreater catalyst change-out operations or shutdowns required by ASME pressure vessel requirements or state boiler codes, or as a result of Malfunction, that prevents the hydrotreater from effectively producing the quantity and quality of feed necessary to achieve established FCCU emission performance.
- c. "Pollutant Reducing Catalyst Additive" shall mean either a NO<sub>x</sub> Reducing Catalyst Additive or a SO<sub>2</sub> Reducing Catalyst Additive.
- d. "SO<sub>2</sub> Reducing Catalyst Additive" shall mean a catalyst additive that is introduced to an FCCU to reduce SO<sub>2</sub> emissions by reduction and adsorption.
- e. "Total Catalyst" shall mean all forms of catalyst added to the FCCU, including but not limited to base catalyst, equilibrium catalyst, and pollutant reducing catalyst.



f. "Total Catalyst Addition Rate" shall mean the Total Catalyst added to an FCCU in pounds per day.

g. "Weight % Pollutant Reducing Catalyst Additive Rate" shall mean:

$$\frac{\text{Amount of Pollutant Reducing Catalyst Additive in Pounds per Day}}{\text{Baseline Total Catalyst Addition Rate}} \times 100\%$$

## 2. Collection of SO<sub>2</sub> Baseline Data.

a. By no later than the dates specified in Section 7 below for each relevant FCCU, Valero shall collect and submit to EPA the baseline data specified below. The baseline data shall include at a minimum the following information for the FCCU, on a daily average basis, for the baseline period:

- a. Regenerator flue gas temperature;
- b. FCCU coke burn rate in pounds per hour;
- c. FCCU feed rate in barrels per day;
- d. FCCU feed API gravity;
- e. FCCU feed sulfur in weight %;
- f. Estimated percentage, and where available, actual percentage of each type of FCCU feed component (*i.e.* atmospheric gas oil, vacuum gas oil, etc.)
- g. Estimated percentage, and where available, actual percentage by volume of the FCCU feed that is hydrotreated;
- h. CO boiler combustion temperature, if applicable;
- i. CO boiler firing rate and fuel type, if applicable;
- j. Total catalyst addition rate and catalyst circulation rates;
- k. FCCU conversion rate;
- l. NO<sub>x</sub> and SO<sub>2</sub> Reducing Catalyst Additive and addition rates, conventional combustion promoter addition rates, and/or Low NO<sub>x</sub> Combustion Promoter addition rates in pounds per day;
- m. Hourly and daily SO<sub>2</sub>, NO<sub>x</sub>, CO, and O<sub>2</sub> concentrations (For Benicia, only total sulfur concentrations shall be provided per the monitoring program described in Section VI of this Decree); and
- n. Any other parameters that Valero identifies as important before the end of the demonstration period.

Upon request by EPA, Valero will submit any additional reasonably available data that EPA

determines it needs.

- b. By no later than the dates specified in Section 7 below for each relevant FCCU, Valero shall submit to EPA a report describing a model to predict the SO<sub>2</sub> concentration and mass emission rate for each FCCU (“the Baseline Report”).

**2. SO<sub>2</sub> Reducing Catalyst Additives - Short Term Trials.**

- a. By no later than the dates specified in Section 7 below, for each relevant FCCU Valero shall submit to EPA, for its approval, a proposal and a protocol for conducting trials to evaluate at least two commercially available SO<sub>2</sub> reducing catalyst additives during the SO<sub>2</sub> catalyst additive trial of the FCCU (“the Additive Proposal Report”).
- b. Valero will propose use of at least two brands of SO<sub>2</sub> Reducing Catalyst Additives that are likely to perform the best in each FCCU. EPA will base its approval or disapproval on its assessment of the performance of the proposed brands of additives in other FCCUs, the similarity of those FCCUs to Valero’s FCCUs, as well as any other relevant factors, with the objective of conducting trials of the brands of SO<sub>2</sub> Reducing Catalyst Additives likely to have the best performance in reducing SO<sub>2</sub> emissions. In the event that Valero submits less than two approvable brands of additives, EPA will identify other approved additives brands to Valero.
- c. Valero shall evaluate at least two additives during the trial. Valero shall submit a report to EPA that describes the performance of each SO<sub>2</sub> catalyst additive evaluated for the FCCU (the “Trial Report and Optimization Protocol”). In the report, Valero will propose

to use the best performing additive as measured by the percentage of SO<sub>2</sub> reduced and the concentration to which SO<sub>2</sub> emissions are reduced in the trials, taking into account all relevant factors. EPA will either approve the proposed additive or approve another additive evaluated by Valero during the trial of the FCCU (the “EPA-approved SO<sub>2</sub> Reducing Catalyst Additive”) for use in the optimization study.

3. **SO<sub>2</sub> Reducing Catalyst Additives - Optimization Study.**

- a. The purpose of the optimization study is to determine the optimized addition rate of the EPA-approved SO<sub>2</sub> Reducing Catalyst Additive according to the procedures described below. Valero shall commence implementation and complete the Optimization Study by no later than the dates specified in Section 7 below for the relevant FCCU.
- b. By no later than the dates specified in Section 7 below for each relevant FCCU, Valero shall submit for EPA approval, a proposed protocol (the “Trial Report and Optimization Protocol”) consistent with the requirements of this appendix for an optimization study to establish the optimized SO<sub>2</sub> reducing catalyst additive addition rates. The protocol will include methods to calculate effectiveness, methods of baseloading, and amount of additive added at each increment.
- c. **Overview.** The Optimized SO<sub>2</sub> Reducing Catalyst Additive Addition Rate will be determined by evaluating SO<sub>2</sub> emissions reductions at three different addition rates.
- d. **The Increments.** The three addition rates or “increments” will be:
  - 5.0 Weight % SO<sub>2</sub> Reducing Catalyst Additive;
  - 7.5 Weight % SO<sub>2</sub> Reducing Catalyst Additive; and
  - 10.0 Weight % SO<sub>2</sub> Reducing Catalyst Additive.



e. **The Procedure.** Valero will successively add SO<sub>2</sub> Reducing Catalyst Additive at each increment set forth above. Once a steady state has been achieved at each increment, Valero will evaluate the performance of the SO<sub>2</sub> Reducing Catalyst Additive in terms of SO<sub>2</sub> emissions reductions. The final Optimized SO<sub>2</sub> Reducing Catalyst Additive Addition Rate will occur at the addition rate, in pounds per day, where either:

- (1) the FCCU meets 25 ppmvd SO<sub>2</sub> (corrected to 0% O<sub>2</sub>) on a 365-day rolling average and 50 ppmvd SO<sub>2</sub> (corrected to 0% O<sub>2</sub>) on a 7-day rolling average, in which case Valero will agree to accept limits of 25 ppmvd SO<sub>2</sub> (corrected to 0% O<sub>2</sub>) on a 365-day rolling average and 50 ppmvd SO<sub>2</sub> (corrected to 0% O<sub>2</sub>) on a 7-day rolling average at the conclusion of the Demonstration Period;
- (2) the addition of SO<sub>2</sub> adsorbing catalyst additive limits the FCCU feedstock processing rate or conversion capability in a manner that cannot be reasonably compensated for by the adjustment of other parameters, the maximum addition rate will be reduced to a level at which the additive no longer interferes with the FCCU processing or conversion rate; provided, however, that in no case, will the maximum addition rate be less than 5.0 weight %; or
- (3) the Incremental SO<sub>2</sub> Pick-up Factor is less than 2.0, where the Incremental SO<sub>2</sub> Pick-up Factor is defined as:

$$\frac{PR_i - PR_{i-1}}{CAR_i - CAR_{i-1}} \text{ where:}$$

PR<sub>i</sub> = Pollutant (SO<sub>2</sub>) reduction rate at increment i in pounds per day from the baseline model

PR<sub>i-1</sub> = Pollutant (SO<sub>2</sub>) reduction rate at the increment prior to increment i in pounds per day from the baseline model

CAR<sub>i</sub> = Total Catalyst Additive Rate at increment i in pounds per day

CAR<sub>i-1</sub> = Total Catalyst Additive Rate at the increment prior to increment i in pounds per day

If the conditions of either (1), (2), or (3) above are not met at any addition rate less than 10.0 weight % SO<sub>2</sub> Reducing Catalyst Additive, then the Optimized Addition Rate will be 10.0

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weight % SO<sub>2</sub> Reducing Catalyst Additive, in pounds per day. In no case will the Optimized Addition Rate will be less than 5.0 weight % SO<sub>2</sub> Reducing Catalyst Additive. The Optimized Addition Rate will not be calculated by interpolation between the increments; it will occur at one of the increments.

If an additive limits the processing rate or the conversion capability in a manner that cannot be reasonably compensated for by adjustment of other parameters, the additive level will be reduced to a level at which the additive no longer causes such limits or effects.

- f. By no later than the dates specified in Section 7 below for each relevant FCCU, Valero shall submit to EPA a written report (the "Optimization Report") identifying the results of the SO<sub>2</sub> Reducing Catalyst Additive Optimization Study for each relevant FCCU.

The Optimization Report shall also include Valero's proposal, for EPA approval, for the optimized addition rate of the EPA-approved SO<sub>2</sub> Reducing Catalyst Additive to be used for the demonstration period. If Valero can demonstrate to EPA's satisfaction that the addition of the selected catalyst additive at the minimum addition rate results in no measurable reduction in SO<sub>2</sub> emissions then Valero may submit a request for EPA approval to discontinue addition of SO<sub>x</sub> reducing additives and to complete the Demonstration Period without the use of any SO<sub>x</sub> reducing additive.

#### **4. SO<sub>2</sub> Reducing Catalyst Additives – Demonstration.**

- a. By no later than the dates specified in Section 7 below for each relevant FCCU, Valero shall commence and complete a demonstration of the EPA-approved SO<sub>2</sub> Reducing Catalyst Additive at the approved optimized addition rate. During the demonstration, Valero shall both physically add SO<sub>2</sub> Reducing Catalyst Additive and

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operate the FCCU, CO boiler (where applicable) and FCCU feed hydrotreater (where applicable) in a manner that minimizes SO<sub>2</sub> emissions, to the extent practicable without interfering with conversion, or processing rates, provided such cannot be reasonably compensated for by adjustment of other operating parameters.

- b. By no later than the dates specified in Section 7 below for each relevant FCCU, Valero shall submit to EPA a report of the results of the Demonstration Period (“the “Demonstration Report”). The Demonstration Report shall include all pertinent data gathered during the Demonstration Period for the categories of information specified in paragraph 2(a) of this Appendix.
- c. At any time prior to the deadline for submission of the Demonstration Report, Valero may notify EPA that it agrees to comply with SO<sub>2</sub> emission limits of 25 ppmvd @ 0% O<sub>2</sub> on a 365-day rolling average basis and 50 ppmvd on a 7-day rolling average basis each at 0% O<sub>2</sub> for a particular FCCU. If Valero makes such a notification, the remaining requirements of this appendix for that particular FCCU shall no longer apply and the limits shall become immediately effective.

##### **5. Establishing SO<sub>2</sub> Emissions Limits.**

- a. Except where Valero has notified EPA of its intent to comply with SO<sub>2</sub> emission limits of 25 ppmvd on a 365-day rolling average basis and 50 ppmvd on a 7-day rolling average basis, at 0% oxygen, Valero will propose, in each Demonstration Report, final 7-day rolling average and 365-day rolling average concentration-based (ppmvd) SO<sub>2</sub> emission limits, at 0% oxygen, for each relevant FCCU. Valero will propose a 7-day rolling average concentration limit that will be numerically twice the concentration of the 365-day rolling average concentration limit. Valero

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may propose alternative emissions limits to be applicable during Hydrotreater Outages, startup of the FCCU, shutdown of the FCCU, or other alternative operating scenarios. Valero will comply with the emission limits it proposes for each FCCU beginning immediately upon submission of the applicable report for that FCCU. Valero will continue to comply with these limits unless and until Valero is required to comply with the emissions limits set by EPA pursuant to the paragraphs below. Upon request by EPA, Valero will submit any additional, reasonably available data that EPA determines it needs to evaluate the demonstration.

- i. EPA will use the data collected about each FCCU during the baseline period, the optimization period, and the demonstration period, as well as all other available and relevant information, to establish limits for SO<sub>2</sub> emissions for each relevant FCCU. EPA will establish a 365-day rolling average concentration-based (ppmvd) SO<sub>2</sub> emission limits at 0% oxygen. EPA will determine the limits based on: (a) the level of performance during the baseline, optimization, and demonstration periods; (b) a reasonable certainty of compliance; and (c) any other available and relevant information. EPA will also establish a 7-day rolling average concentration limit that will be numerically twice the concentration of the 365-day rolling average concentration limit.
- ii. EPA will notify Valero of its determination of the concentration-based SO<sub>2</sub> emissions limit and averaging times for each FCCU, including how and whether emissions during Hydrotreater Outages are included in the 365-day rolling average. EPA may establish alternative emissions limits to be applicable during Hydrotreater Outages, startup of the FCCU, shutdown of the FCCU, or other alternative

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operating scenarios. If EPA agrees with Valero's proposed limits, Valero will continue to comply with these limits. If EPA proposes different limits that Valero does not dispute within thirty (30) days of receiving notification from EPA, Valero will comply with the EPA-established limits by no later than thirty (30) days after notice. If Valero disputes the EPA-established limits, Valero will invoke the dispute resolution provisions of this Decree by no later than thirty (30) days after EPA's notice of the limits. During the period of dispute resolution, Valero will continue to add SO<sub>2</sub> Reducing Catalyst Additives at the optimized rates and comply with any approved Hydrotreater Outage plan.

- iii. SO<sub>2</sub> emissions during periods of startup, shutdown, or Malfunction of an FCCU controlled by catalyst additives, or during periods of Malfunction of a Pollutant Reducing Catalyst Additive system will not be used in determining compliance with the short-term SO<sub>2</sub> emission limits established pursuant to this appendix, provided that during such periods Valero implements good air pollution control practices to minimize SO<sub>2</sub> emissions.

#### **6. Monitoring Requirements for Benicia FCCU**

- i. Special monitoring provisions are required for the SO<sub>2</sub> reducing catalyst trial on the Benicia FCCU because this unit utilizes a combined CO Boiler for combustion of flue gas from the Refinery's FCCU and Fluid Coker. Requirements for submittal of a site specific monitoring plan for the Benicia FCCU catalyst additive trial with EPA approval are specified in Paragraph 93 of the Decree. Baseline data collection for the Benicia FCCU will begin by March 31, 2006 or 180 days after EPA's



approval of the site specific monitoring plan, whichever is later.

## 7. Catalyst Additive Schedule Summary

The schedule for the SO<sub>2</sub> reducing catalyst additive protocol at the five FCCUs using SO<sub>2</sub>

reducing catalyst additive is as follows:

	<u>McKee</u>	<u>Krotz Springs</u>	<u>Benicia</u>	<u>Denver</u>	<u>Corpus Christi East</u>	<u>Wilmington</u>
Start to collect baseline data	6-30-06 (Note 2)	12-31-06 (Note 3)	3-31-06	12-31-05	12-31-05	12-31-05
Submit Additive Proposal Report	12-31-06	6-30-07	9-30-06	6-30-06	6-30-06	6-30-06
Complete baseline data collection	6-30-07	12-31-07	3-31-07	12-31-06 (Note 1)	12-31-06 (Note 1)	12-31-06 (Note 1)
Submit Baseline Report and start Trials	9-30-07	3-31-08	6-30-07	3-31-07	3-31-07	3-31-07
Complete Trials	3-31-08	9-30-08	12-31-07	9-30-07	9-30-07	9-30-07
Submit Trial Report and Optimization Protocol	5-31-08	11-30-08	2-29-08	11-30-07	11-30-07	11-30-07
Begin Optimization	8-31-08	2-28-09	5-31-08	2-29-08	2-29-08	2-29-08
Complete Optimization	5-31-09	11-30-09	2-28-09	11-30-08	11-30-08	11-30-08
Submit Optimization Report	8-31-09	2-28-10	4-30-09	2-28-09	2-28-09	2-28-09
Begin Demonstration Period	10-31-09	4-30-10	6-30-09	4-30-09	4-30-09	4-30-09
Complete Demonstration Period	4-30-11	10-31-12	3-31-10	2-28-11	2-28-11	2-28-11
Submit Demonstration Report	6-30-11	12-31-12	5-31-10	4-30-11	4-30-11	4-30-11

If EPA has not approved any of the items requiring its approval under this protocol in a timely fashion, then subsequent deadlines may be modified as agreed to by the parties.

### Notes:

1. Baseline data will be collected for all three FCCUs, addressed in Paragraphs 69-72 of the Decree, but the catalyst protocol will only be completed for the two FCCUs that are not chosen for installation of an FCCU scrubber.

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2. The protocol start date for the McKee FCCU is based on a scheduled DCS system upgrade necessary to collect and process data. In addition, the protocol start date is after the start up of a new gasoline desulfurization unit which will result in a varied crude slate and a heavier FCCU feedstock.

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